

**(19) World Intellectual Property
Organization
International Bureau**



(43) International Publication Date
24 June 2004 (24.06.2004)

PCT

(10) International Publication Number
WO 2004/052530 A1

(51) International Patent Classification⁷: B01J 19/00

(21) International Application Number:
PCT/US2003/038373

(22) International Filing Date: 4 December 2003 (04.12.2003)

(25) Filing Language: English

(26) **Publication Language:** English

(30) Priority Data:
10/313,334 5 December 2002 (05.12.2002) US

(71) Applicant (for all designated States except US): UOP LLC [US/US]; 25 East Algonquin Road, Des Plaines, IL 60016 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): KARLSSON, Arne [SE/NO]; SINTEF, 124 Blindern, N-0314 Oslo (NO). KRAWCZYK, Mark, A. [US/US]; UOP LLC, 25 East

Algonquin Road, Des Plaines, IL 60016 (US). ALEXANIAN, Ara, J. [US/US]; UOP LLC, 25 East Algonquin Road, Des Plaines, IL 60016 (US). AKPORIAYE, Duncan, E. [GB/US]; UOP LLC, 25 East Algonquin Road, Des Plaines, IL 60016 (US). DAHL, Ivar, M. [NO/NO]; SINTEF, 124 Blindern, N-0314 OSLO (NO).

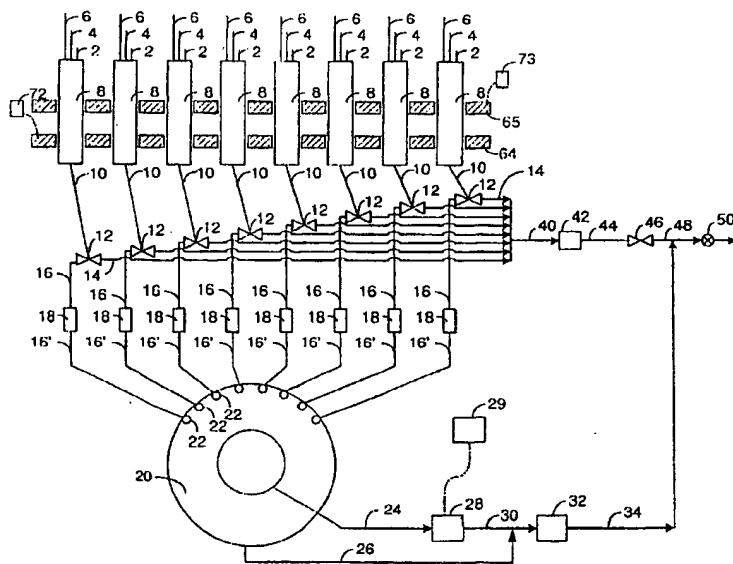
(74) Common Representative: UOP LLC; John G. Tolomei, Assistant Secretary-Patent Matters, 25 East Algonquin Road, Des Plaines, IL 60016 (US).

(81) **Designated States (national):** AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,

[Continued on next page]

(54) Title: ELEVATED PRESSURE APPARATUS AND METHOD FOR GENERATING A PLURALITY OF ISOLATED EFFLUENTS



(57) Abstract: An apparatus and a method for rapidly generating a plurality of isolated effluents have been developed. A specific embodiment involves screening a plurality of solids through simultaneously contacting the members of the plurality with a fluid, sampling the resulting fluids, and processing the resulting fluids to, for example, determine changes as compared to the feed fluid or as compared to other resulting fluids.

WO 2004/052530 A1

WO 2004/052530 A1



ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE,
SI, SK, TR), OAPI patent (BI, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

— *before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments*

Published:

— *with international search report*

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

**"ELEVATED PRESSURE APPARATUS AND METHOD FOR
GENERATING A PLURALITY OF ISOLATED EFFLUENTS"**

BACKGROUND OF THE INVENTION

[0001] The present invention relates to an apparatus and a method for rapidly
5 generating a plurality of isolated effluents. A specific embodiment involves screening a
plurality of solids at elevated pressure through simultaneously contacting the
members of the plurality with a fluid, sampling the resulting effluents, and processing
the resulting effluents to, for example, determine changes as compared to the feed
fluid or as compared to other resulting effluents.

[0002] Combinatorial chemistry approaches have been applied to catalyst testing
10 in an attempt to expedite the testing process. With the growing number of materials
being synthesized combinatorially, more efficient methods of evaluating the materials
are needed. Especially needed are combinatorial methods for the evaluation of solids
that are designed to keep pace with the speed of combinatorial synthesis. Some
15 commercial processes have operated using multiple parallel reactors where the
products of all of the reactors are combined into a single product stream; see US-A-
5,304,354 B1 and US-A-5,489,726 B1. Another patent, US-A-6,149,882 B1 teaches
an apparatus having a plurality of vessels and valves and conduits for sequentially
sampling the effluent of the vessels or a sample probe positioned next to the effluent
20 to transport sampled fluid to a detector.

[0003] Applicants have developed a combinatorial method and apparatus
particularly suited for the generation of a plurality of independent effluents. The
effluents are generated in parallel and are kept isolated from one another. The
effluents may be further processed by, for example, analyzing the composition of the
25 effluents, by further reacting the effluents, by further treating the effluents, and the like.
Multiple solids are contacted with a feed fluid in parallel with the resulting effluents
being sampled and then analyzed for changes as compared to the feed fluid. The
apparatus and method is particularly beneficial when generating the plurality of
effluents at elevated pressures. Furthermore, the apparatus is adaptable for
30 generating the effluents from the combination of gas feed and liquid feeds. A diluent
gas may also be introduced to the vessels. The parallel reactions and the analyses
provide a means for the high throughput evaluation of multiple solids or mixtures of
solids.

SUMMARY OF THE INVENTION

[0004] One purpose of the present invention is to provide an apparatus for generating a plurality of effluents where the apparatus consists of a multiplicity of vessels containing solids with each vessel having an inlet and an outlet,
5 a multiplicity of effluent conduits in fluid communication with the outlets of the vessels each effluent conduit which divides into a sampling conduit and a vent conduit, each sampling conduit containing a restrictor, at least one sampling valve in fluid communication with the sampling conduits, a bypass conduit and a processing conduit in fluid communication with the sampling valve, and a processing device in fluid
10 communication with the processing conduit from the sampling valve. The invention is particularly useful to evaluate a plurality of solids at elevated pressures.

[0005] Another purpose of the present invention is to provide a method of generating a plurality of effluents where a plurality of solids are contained in a set of vessels with each vessel having an inlet and an outlet. The solids are contacted,
15 simultaneously, at elevated pressure, with a feed fluid to generate vessel effluents. Each effluent is split into a sample portion and a vent portion. The pressure of the sample portions is reduced and the sample portions are routed to a sampling valve. A sample portion is selected using the sampling valve and the selected sample portion is processed. The further processing may be analyzing the vessel effluents to
20 determine changes in the vessel effluents as compared to the feed fluid or as compared to other vessel effluents. Such analyses may be particularly useful in evaluating a plurality of solids.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] FIG.1 is a schematic drawing of the feed system of the embodiment of the
25 invention shown in FIG. 2.

[0007] FIG. 2 is a schematic drawing of a portion of one embodiment of the invention, an apparatus for rapidly screening solids. The figure shows only the first of multiple banks of reactors.

DETAILED DESCRIPTION OF THE INVENTION

30 [0008] An apparatus and a method are provided for combinatorial generation of a plurality of effluents. In general terms, a feed fluid is contacted simultaneously with a plurality of solids where each of the solids is housed in an individual vessel in order to

generate vessel effluents. The feed fluid may be a gas or a gas and a liquid, and the vessel effluents may be mixed with a diluent gas. The contacting may be conducted at elevated temperature and elevated pressure. Each vessel effluent is separated into a sample portion and a vent portion. The vent portions may be combined and directed to waste. The pressure of the sample portions are reduced and directed to a sampling valve. Using the sampling valve, a single sample portion is selected for further processing. For example, when screening a plurality of solids, the sample portion selected is introduced into, for instance, one or more gas chromatographs for analysis. Changes in the effluents as compared to the feed or to each other are used to determine properties of the plurality of solids being tested. The results of the analysis may also indicate those solids whose performance warrants further investigation. Sample portions that are not selected are combined into a bypass line which bypasses the processing device. The bypass line is connected to the combined vent portions line.

[0009] The plurality of effluents generated by the subject invention are further processed by, for example without limitation, further reacting the effluents, separating the effluents, treating the effluents with an adsorbent, analyzing the effluent, and the like. Any relevant processing device may be used in the processing; reactors, adsorbers, analytical instrumentation, etc. The discussion herein will focus on analyzing the plurality of effluents as is useful in screening a plurality of solids.

[0010] The apparatus and method of the present invention may be used to screen the plurality of samples for any property that can be determined through measuring or monitoring the changes between the feed fluid and the effluent or between the multiple effluents. For example, catalytic activity of a solid may be evaluated by analyzing the concentration of the reactants in the feed fluid as compared to the reactants and products of each reactor effluent. With the present invention, those solids showing the greatest conversion to the products or perhaps the greatest selectivity to the desired product could be determined expediently. Similarly, adsorptivity of solids may be evaluated by comparing the concentration of an adsorbate in a feed stream with the concentration of the same adsorbate in each of the reactor effluents. Those solids having the greatest reduction in adsorbate from the feed concentration to the effluent concentration may be quickly identified for further testing and investigation. It is also contemplated that a property of interest may be

determined by comparing the effluents to each other as opposed to, or in addition to, the feed fluid. An important benefit of the present invention is that such identifications can be produced rapidly for a large number of samples. In the same amount of time historically required to evaluate a single solid, with the present invention a multiplicity of solids can be evaluated.

[0011] The present invention is particularly beneficial in applications where the fluid(s) are contacted with the solids at operating conditions that include elevated pressures. For example, pressures ranging from 345 kPag (50 psig) to 3447 kPa (500 psig) are typical for some applications. Additionally, the present invention is beneficial where both a liquid feed and a gas feed are introduced to the vessels containing the plurality solids. Finally, the present invention is especially beneficial in applications where a diluent gas is to be mixed with the effluents of the vessel. In a specific embodiment, the diluent gas is mixed with effluents of a treatment zone within the vessel before the effluents exit the vessel.

[0012] For ease of explanation, the process and apparatus will be described herein as a 48-reactor system where the reactors are grouped into six banks containing eight reactors in each bank. FIG. 1. shows the source fluids and the source fluid distribution. FIG. 2 shows only a portion of the source fluid distribution and only the first bank of eight reactors and associated equipment. The other five banks of eight reactors each, and the equipment associated with each bank of reactors, are not shown. Although the vessels are referred to throughout as "reactors" it must be emphasized that vessels other than reactors are suitable for the present invention. "Reactors" are merely used in reference to a specific embodiment of the invention.

[0013] Turning to FIG. 1, the process begins with one or more source fluids in containers 60 and 68. At least one source fluid is preferably gaseous, and the other may be liquid or gas. In this example, the source fluid from container 60 is a gas and the source fluid from container 68 is a liquid. The gas fluid may be saturated with other components. For purposes of this description, the gas is contained within container 60 which is a cylinder. The pressure of the source gas is maintained above the reaction pressure and may be stepped down through, for example, a series of reducing valves. The liquid may be from a pressurized reservoir tank and may be a mixture of two or more liquids. The liquid may be maintained at reaction pressure using inert gas such as helium, nitrogen or argon, or the liquid could be maintained at a pressure lower than reaction pressure and pumped to a higher pressure when necessary.

[0014] A main gas conduit 62 directs gas from cylinder 60 to be split into eight individual gas feed lines 2. Note that in alternative embodiments, main gas conduit 62 can be connected to a selector that operates to select gas from two or more reservoirs. It is preferred that the stream in the main gas conduit 62 be allowed to
5 separate into the eight individual gas feed lines 2 by passing through, for example, branch connectors. The purpose of the branch connectors is merely to split the source fluid stream into eight portions. It is not necessary that the eight separated portions be regulated as to mass flow at this point. After the separation via branch connectors, each individual gas feed line is equipped with a mass flow controller 66. The mass
10 flow controllers are used to control the flow of the gas feed to the reactor vessels. Similarly, a main liquid conduit 70 directs liquid from reservoir 68 to be split into eight individual liquid feed lines 4. Again, the purpose of the branch connectors is merely to split the source liquid stream into eight portions, and not to regulate mass flow at this point. After the separation via branch connectors, each individual liquid feed line is
15 equipped with a mass flow controller 74. The mass flow controllers are used to control the flow of the liquid feed to the reactor vessels. Because each of the feed lines 2 is equipped with an individual mass flow controller, the split of the gas of line 62 into lines 2 and the split of the liquid of line 70 into lines 4 is not controlled. Pressure transducers may be used to monitor the pressure of any of the fluid in lines 62, 2, 70
20 and 4.

[0015] FIG. 1 further shows the optional diluent gas source 76. The diluent gas is mixed with the effluents to prevent components in the effluent from condensing in the conduits and fouling the effluent lines. The diluent gas may also be used to maintain sufficient pressure in the reactor and streams. As with the gas fluid discussed above,
25 the pressure of the diluent gas at the source is preferably above the reaction pressure. The diluent gas is conducted from source 76 through conduit 78 and to valve 80. Valve 80 splits the diluent gas into eight portions that are conducted in lines 6. Other devices such as a manifold with restriction orifices or individual restrictors may also be successfully employed in the present invention. Alternatively, each individual diluent
30 gas line may be equipped with a mass flow controller. Restrictor-type splitting of the diluent gas is less costly than individual mass flow controllers, and the need to vary the diluent gas flow between the different reactors is lower thereby rendering the restrictor-type splitting of the gas fluid to be the preferred embodiment. Capillary-type or capillary tube restrictors are suitable devices for distributing the diluent fluid into

portions.

[0016] It is preferred that the diluent gas be mixed with gas resulting from the feed contacting the solids at a point after contacting the solids and before the effluent exits the vessel. It is possible to have the diluent gas follow the same flow path as the feed, but then the treatment zone of the vessel may need to be enlarged to accommodate additional fluid flow. Also, using the same flow path may change the reaction characteristics such as conversion, selectivity, and yield since with the addition of the diluent, the reactant concentrations were altered. With the diluent gas routed around the treatment zone of the vessel but yet mixing with the resulting effluent at a location near to the treatment zone and preferably within the vessel, the dilution function is accomplished without enlarging the treatment zone. In addition, the location is most likely at a temperature near to the treatment temperature thereby eliminating the need for heat traced lines to conduct the effluent to a location for mixing with the diluent.

[0017] Since each gas feed line 2 and each liquid feed line 4 to each of the reactor vessels has its own individual mass flow controller, the system is very versatile. For example, each of the gas feed lines 2 may be independently controlled via the mass flow controllers 66 to allow the same space velocity of the gas to pass through each of the gas feed lines, or the mass flow controllers 66 may be independently controlled so that a different space velocity of the gas feed passes through one or more of the gas feed lines 2. At the same time, each of the liquid feed lines 4 may be independently controlled via the mass flow controllers 74 to allow the same space velocity of the liquid to pass through each of the liquid feed lines, or the mass flow controllers 74 may be independently controlled so that a difference space velocity of the liquid feed passes through one or more of the liquid feed lines 4. The particular application and the data desired or variables being investigated are factors to be considered when determining the flow rates of the fluids to the reactor vessels.

[0018] Fig. 1 shows a single gas feed source, 60, and a single liquid source, 68, but in other embodiments additional sources may be employed. A set of six selector valves (not shown) are connected via branch connectors to each of the fluid source lines; i.e., each valve in the set of six is connected via branch connectors to each of the fluid source lines. In the present example, six selector valves are required because there are six banks of reactors. In other applications, the number of selector valves may vary. The purpose of the selector valve is to allow for the selection of the source fluid that will be conducted to the reactors. In this example, the selector valves

for the gases are preferably 8-port valves, although various other devices may be used. The valves are positioned so that the selected source fluids are able to pass through the valves while the source fluids that are not selected are blocked and unable to pass through the valves. The selection valve and corresponding source
5 fluids allow the solids to be pretreated using a variety of gasses, oxidative, reductive, or neutral, as well as providing the co-feed containing reactants.

[0019] From the mass flow controllers 66 and 74, the gas feed stream in lines 2 and the liquid feed stream in lines 4 are simultaneously introduced to the individual reactor vessels 8. The reactors, 8, may be of any type used in combinatorial
10 evaluations, with preferred reactors being of the type described in U.S. Application Nos. 10/095,879, 10/095,934, and 10/095,395. Other suitable reactors include EP 1108467 A2, US-A-6,342,185 and US-A-6,327,344. The number of vessels, e.g., reactors in this embodiment, making up the multiplicity may vary from two vessels to hundreds of vessels. It is preferred to have at least eight or at least sixteen vessels in
15 the multiplicity and it is most preferred to have forty-eight vessels in the multiplicity. Diluent gas in lines 6 may also be simultaneously introduced to vessels 8. However, it is preferred that diluent gas be routed around the reaction zone of the vessels 8 and mix with the effluent of the reaction zone before exiting the vessel. A preferred reactor that allows for the diluent gas to bypass the reaction zone is found in U.S. Application
20 Nos. 10/095,879, 10/095,934, and 10/095,395. Such a configuration prevents unnecessarily large volumes from flowing through the reaction zones, while at the same time providing a mechanism to prevent components in the effluent of the reaction zone from condensing in the lines. Fouling or plugging of the effluent lines can result in a failure of the system to operate properly and possibly false results.

[0020] The vessels house solids that may interact with the feed streams. For
25 example, the reactors may house catalysts that catalyze a chemical reaction and yield products, or the reactors may house adsorbents that adsorb one or more components from the source fluid. It is within the scope of the invention that the reactor may house a mixture of catalyst and adsorbent. The solids of interest may be present as solid
30 particles or may be supported by solids. Each of the reactors may contain different solids, different mixtures of solids, the same compositional mixture of solids where the components are in different ratios, or the like. Replicates may be included within the array of solids. Although not necessary, typically, the solids will be present in a fixed bed. The reactor feed streams will flow through the interstices of the fixed bed

providing contact between the solid and the reactor feed stream. The reactors may be associated with at least heater, 64, having a controller, 72, to provide controlled heat to the reaction zone of the reactors. Similarly, the reactors may be associated with heater 65 having controller 73 to provide controlled heater to another zone of the reactors such as an evaporation zone. Alternatively, individual heaters may be employed with each heater associated with a specific vessel.

[0021] The effluent from each of the reactors is conducted simultaneously, yet separately, in lines 10 to gas splitting devices 12. Gas splitting devices 12 can be, for example, SGE valves or branch connectors. FIG. 2 shows gas splitting devices 12 as two-way valves which direct flow into two conduits in one position and blocks flow in the other position. In this particular example, as the effluent passes through gas splitting devices 12, the bulk of each effluent stream is directed into vent lines 14 and a smaller portion of each effluent is directed into sample lines 16. The amount of effluent directed into sample lines 16 and vent lines 14 depends upon the specific application. However, factors such as the amount of effluent necessary for further processing are considered. For example, if the further processing is compositional analysis using gas chromatography, enough effluent should be directed to the sample lines 16 so that proper technique may be used in the gas chromatographic analysis. The plurality of vent lines 14 can be combined into a single vent line 40 which is equipped with vapor-liquid disengaging volume 42 and back pressure regulator 46. For ease of understanding, the vapor-liquid disengaging volume 42 will be referred to as a preferred embodiment of knock-out pot or condenser 42. As effluent passes from line 40 and through knock-out pot 42, liquid is separated from gaseous material. Knock-out pots are known in the industry and will not be described in detail herein. The preferred knock-out pot temperature is below ambient. This design allows for pressure regulation of the gaseous content of the effluent. The gaseous material from knock-out pot 42 after passing through back-pressure regulator 46 may be combined with line 24 and the combined stream passed to moisture analyzer 50.

[0022] Sample lines 16 are equipped with pressure reducing devices such as restrictors 18 that operate to reduce the pressure in the lines and to restrict the amount of fluid passing through to an appropriate amount. The pressure in lines 16 between gas splitting devices 12 and restrictors 18 is near to the reaction pressure. After passing through the restrictors 18, the effluent in lines 16', between restrictors 18 and sampling valve 20, is at a reduced pressure as compared to the pressure in lines

16 and preferably close to atmospheric pressure. The pressure may still be elevated slightly above atmospheric to ensure the flow continues through the system according to the general principal that fluid flow is generated from an area of high pressure to an area of lower pressure. The present system is particularly advantageous when the further processing of the effluents require a pressure less than the pressure used in the reaction vessels 8. For example, when the further processing is analytical analysis such as near-IR, FTIR, etc., which is conducted at a pressure less than the reaction pressure, the present system is readily adaptable to provide the stream to be analyzed at a pressure suitable to the analytical method.

10 **[0023]** Reduced-pressure sampling lines 16' carry the effluents to a sampling valve 20. Each of the sampling lines 16' is connected to an individual port of sampling valve 20. Sampling valve 20 allows for the effluent in one of the sampling lines 16' to be selected for further processing with the rest of the effluents in sampling lines 16' bypassing the additional processing step. Sampling valve 20 may be cycled through
15 all of its positions so that the effluent in each sampling line 16' is selected in sequence for additional processing. How the cycling is timed is dependent upon the particular application and may be quite dependent upon the nature of the additional processing. For example, when the additional processing is analysis of the effluent using gas chromatography, the cycle time of the valve may be dependent upon the time needed
20 to complete the chromatographic analysis. It is within the scope of the present invention to utilize sampling valves that simultaneously select two or more effluents for parallel additional processing when multiple processing devices are available. It is preferable that each selected effluent remain isolated from other effluents until the additional processing is completed. The exact type of valves used for sampling valve
25 20 will vary with the application, suitable examples include Valco high temperature and high pressure valves. The valves may be any type of device or valve that allows for a selection of at least one fluid from a multiple of fluid flows with the selected fluid flow directed to a first conduit and the remainder of the fluid flows combined and directed to a second conduit.

30 **[0024]** The selected effluent is directed from sampling valve 20 in line 24 to a processing device 28. An interface may be used to allow for a plurality of processing devices. The processing device may be any device used to treat or measure the effluent such as analytic systems or detectors. For ease of explanation, a gas chromatograph will be the analytical detection device described herein. However,

other analytical techniques such as liquid chromatography, infrared spectroscopy, uv-vis spectroscopy, ultraviolet spectroscopy, visible spectroscopy, fluorescence spectroscopy, infrared thermography, nuclear magnetic resonance, paramagnetic resonance, X-ray adsorption, X-ray photoelectron spectroscopy, Raman spectroscopy and combinations thereof may be similarly employed. Other detectors include ion selective electrodes, potentiometric devices, and photo oxidation analyzers. Other processing devices besides a detector may be used to process the isolated effluents. A reactor may be used to further react the effluents, a separator may be used to separate the effluents, or a treatment vessel containing, for example, an adsorbent may be used to treat the effluents. The processing device may be controlled by a microprocessor 29 which may also store any data generated by the processing device. The effluent from the processing device 30 is passed to knock-out pot 32 to remove liquid and the resulting gas is flowed through line 34 and preferably added to the combined vent effluent in line 48. In other embodiments, the resulting gas flowed through line 34 may be, for example, vented independently of combined vent effluent in line 48.

[0025] In this example, the reactor vessel effluents in lines 16' that are not selected for further processing are combined by sampling valve 20 into line 26. The effluents in line 26 are combined with line 30 and introduced to knock-out pot 32 to condense liquid, and the resulting gas stream is flowed through line 34 and added to the combined vent effluents in line 48. Again, alternative embodiments do not require the resulting gas stream flowed through line 34 to be added to the combined vent effluents in line 48. Depending upon the compounds present in the system, vent effluent may be treated to remove, convert, or neutralize specific components before being vented. Periodically, the knock-out pots 42 and 32 may be emptied of collected liquid.

[0026] A trace of the path of a single set of feeds through the system of FIG.2 is as follows. Gas feed in line 2, liquid feed in line 4, and diluent gas in line 6 are introduced at elevated pressure to reactor 8. Reactor 8 contains catalyst and has an evaporation stage to evaporate the liquid feed and mix with the gas feed so that the combined feeds in a gaseous state are contacted with a catalyst to generate an effluent. The evaporation stage of reactor 8 is heated by heater 65 and reaction stage of reactor 8 is heated by heater 64. After contacting the catalyst, the reaction stage effluent is diluted with diluent gas in reactor 8. The reactor effluent is conducted in line 10 to gas

splitter 12 where a portion of the effluent is directed to line 14 to be vented, and a smaller portion of the effluent is directed to line 16 for further processing. Line 16 is equipped with restrictor 18 to reduce the pressure of the reactor effluent. The reactor effluent of line 16', now at a reduced pressure, is introduced to a port of sampling valve 20. If the cycle position of sampling valve 20 is such that the port of interest is selected, the reactor effluent is directed through line 24 and into a processing device 28. As an example, processing device 28 may be a gas chromatograph. In this embodiment, after processing, the processing device effluent is conducted in line 30 to a knock-out pot 32 for removal or condensation of liquid. The resulting gas stream from knock-out pot 32 is flowed through line 34 and added to the vent effluents in line 48. If, on the other hand, the cycle of sampling valve 20 is such that the port of interest is not selected, the reactor effluent is combined with other non-selected effluents and the combined effluents are directed through line 26 adding with line 30 downstream of processing device to knock-out pot 32 for removal or condensation of liquid. The resulting gas stream from knock out pot 32 is flowed through line 34 and added to the vent effluents in line 48.

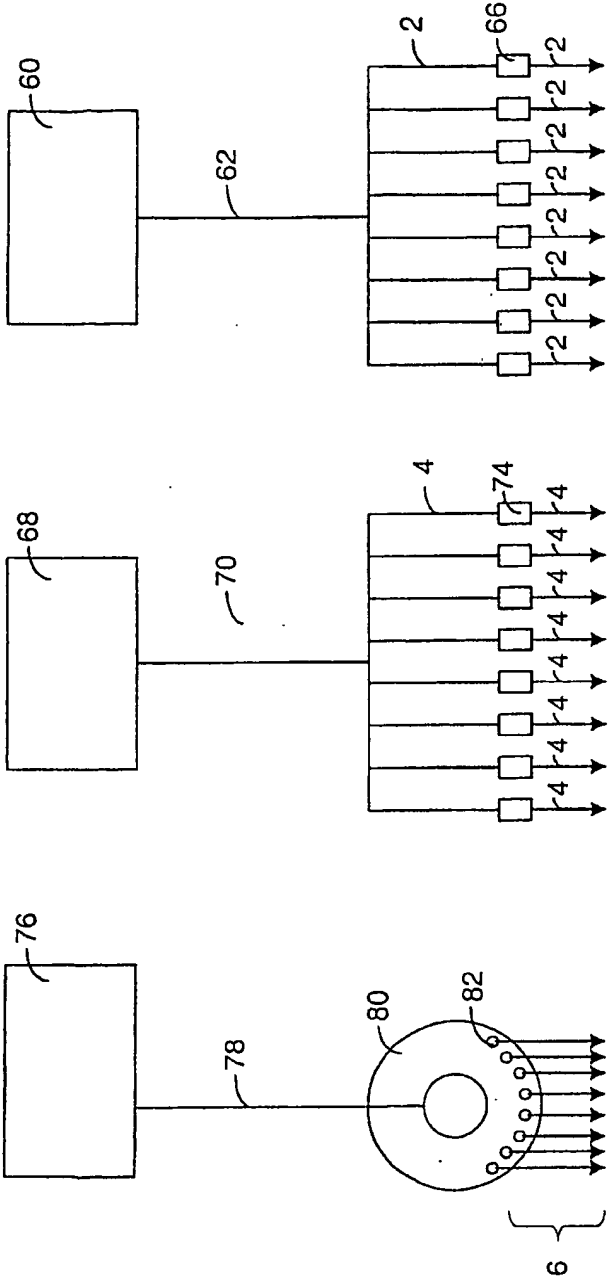
[0027] The portions of the reactor effluents in lines 14 are combined into a single vent effluent 40 which is passed to knock-out pot 42 for the removal of liquid. The resulting gas stream in line 44 is reduced in pressure by back-pressure regulator 46 to form a reduced-pressure combined vent effluent stream 48. The back-pressure regulator 46 in combination with the restrictors 18 and the sources 60, 68 and 76 operate to control the pressure within the reactors and the flow of fluid through the system. Typical pressures the system may be expected to operate within range from 345 kPag (50 psig) to 3447 kPag (500 psig) and different restrictors and back-pressure regulators may be selected depending upon the particular pressure selected.

CLAIMS:

1. An apparatus for generating a plurality of effluents comprising:
 - a) a multiplicity of vessels (8) containing solids, each vessel having an inlet and an outlet;
 - 5 b) a multiplicity of effluent conduits (10) in fluid communication with the outlets of the vessels (8) each effluent conduit further in fluid communication with a sampling conduit (16) and a vent conduit (14); each sampling conduit containing a pressure reducing device (18);
 - 10 c) at least one sampling valve (20) in fluid communication with the sampling conduits;
 - d) a bypass conduit (26) and a processing conduit (24) in fluid communication with the sampling valve (20); and
 - e) a processing device (28) in fluid communication with the processing conduit (24) from the sampling valve (20).
- 15 2. The apparatus of Claim 1 wherein the bypass conduit (26) further comprises a vapor-liquid disengaging volume (32).
3. The apparatus of Claim 1 wherein the processing device (28) is selected from the group consisting of a detector, a reactor, and a treatment vessel.
4. The apparatus of Claim 1 further comprising a multiplicity of feed conduits (2, 4)
20 in fluid communication with the multiplicity of vessels (8) and a multiplicity of diluent conduits (6) in fluid communication with the multiplicity of vessels (8), preferably wherein each feed conduit and each diluent conduit further comprises a mass flow controller (66,74).
5. The apparatus of Claim 1 wherein the vessels (8) have an evaporation zone
25 and a reaction zone, and are comprised of a housing, a sleeve and an insert; and wherein the apparatus further comprises at least one heater (64) located proximate to the vessels and an associated temperature control system (72) for regulating the temperature of the vessels.
6. A method of generating a plurality of effluents comprising:
30 a) simultaneously contacting, at elevated pressure, at least one feed fluid (2, 4) with a plurality of solids to generate a plurality of effluents (10);

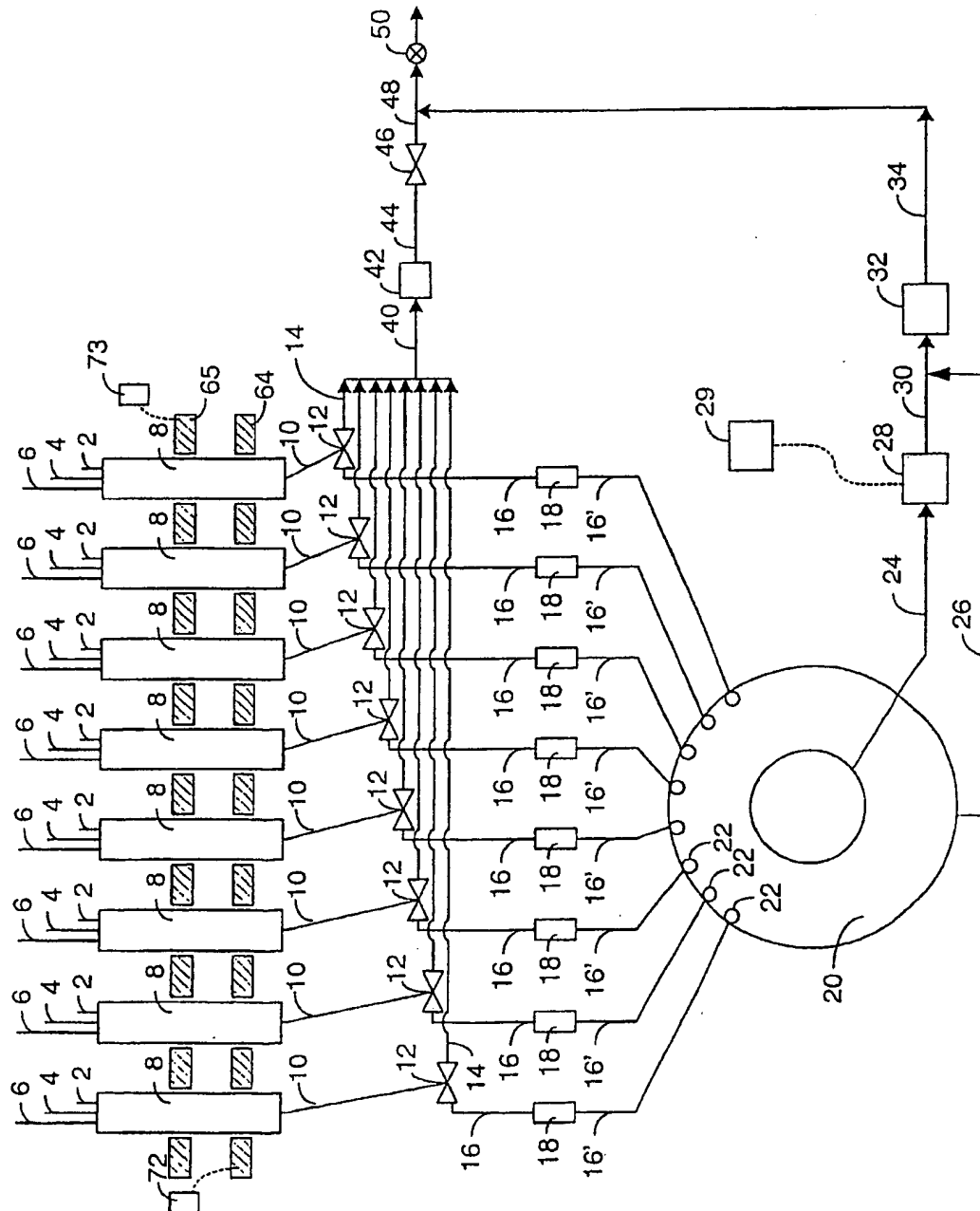
- b) separating each effluent into a sample portion (16) and a vent portion (14);
 - c) reducing the pressure (18) of the sample portions (16) and routing the sample portions (16') to a sampling valve (20); and
 - 5 d) selecting a sample portion (24), using the sampling valve (20), and processing (28) the selected sample portion (24).
7. The method of Claim 6 further comprising combining at least two of the vent portions (14) to form a combined vent portion (40), passing the combined vent portion (40) through a vapor-liquid disengaging volume (42) and reducing the pressure (46) of
- 10 the combined vent portion (44).
8. The method of Claim 6 wherein the feed fluid comprises a gas feed (2) and a liquid feed (4) and a diluent fluid (6) is mixed with each effluent (10).
9. The method of Claim 6 wherein the processing (28) comprises analyzing the effluents (10, 16, 24) and determining changes in the effluents (10, 16, 24) as
- 15 compared to the feed fluid (2, 4).
10. The method of Claim 6 wherein the processing (28) comprises further treating the effluents (24).

Fig. 1



2/2

Fig. 2



INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 03/38373

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J19/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 072 886 A (INST FRANCAIS DU PETROL) 31 January 2001 (2001-01-31)	1-4,6-10
Y	abstract page 1, paragraph 1 page 5, paragraph 30 - paragraph 31 page 6, paragraph 43; figure 1	5
X	WO 01/59463 A (CORMA CANOS AVELINO ;UNIV VALENCIA POLITECNICA (ES); CONSEJO SUPER) 16 August 2001 (2001-08-16)	1-4,6-10
Y	abstract page 18, line 23 -page 20, line 9; figure 1	5
	--- -/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

19 May 2004

Date of mailing of the international search report

01/06/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Nazario, L

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/38373

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 368 865 B1 (DAHL IVAR M ET AL) 9 April 2002 (2002-04-09) abstract column 11, line 34 -column 12, line 17; figure 1 ---	5
A	US 4 099 923 A (MILBERGER ERNEST C) 11 July 1978 (1978-07-11) abstract column 3, line 47 - line 63 column 5, line 36 -column 7, line 34 column 8, line 42 - line 50; figures ---	1-10
A	US 2002/086791 A1 (IGLESIA ENRIQUE ET AL) 4 July 2002 (2002-07-04) abstract page 5, paragraph 47 -page 7, paragraph 64; figure 2 -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/38373

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1072886	A	31-01-2001	FR 2795513 A1	29-12-2000
			CA 2312523 A1	28-12-2000
			EP 1072886 A1	31-01-2001
			US 6551832 B1	22-04-2003
WO 0159463	A	16-08-2001	ES 2166310 A1	01-04-2002
			EP 1273919 A1	08-01-2003
			WO 0159463 A1	16-08-2001
			JP 2003522949 T	29-07-2003
			US 2003040116 A1	27-02-2003
US 6368865	B1	09-04-2002	NONE	
US 4099923	A	11-07-1978	NONE	
US 2002086791	A1	04-07-2002	WO 03020417 A1	13-03-2003
			US 2003078740 A1	24-04-2003
			US 2002128872 A1	12-09-2002